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Electrochemical properties of gold nanoparticles assembly at polarised liquid|liquid interfaces

Nathalie Younan, Mohamad Hojeij, Lydie Ribeaucourt, Hubert H. Girault *

Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland

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ABSTRACT

Capacitance measurements of a polarised liquid|liquid interface show that the capacitance of the interface increases in the presence of an adsorbed monolayer of citrate-coated gold nanoparticles. This unusual observation can be explained by an increase of the interfacial charge density or by an increase of the interfacial corrugation. This study shows that capacitance measurements provide a method to monitor metallic film formation at ITIES.

1. Introduction

Polarised liquid|liquid interfaces can be functionalised by nano-objects such as metallic or semiconducting nanoparticles. Indeed, soft liquid|liquid interfaces represent a defect free support for nanoparticles and nanoparticle assemblies. Since the early work of Efrima et al. who showed in 1988 the formation of silver metal-like films at the water|dichloromethane interface [1], many publications have shown that many different types of films could be formed at liquid|liquid interfaces as recently reviewed by Böker et al. [2].

In the case of gold nanoparticles, the formation of a film at the interface is not always spontaneous and it has been shown that hydrophilic gold nanoparticles (Au NPs) can be assembled into 2D arrays at water|oil interfaces by adding a low-dielectric solvent, such as methanol or ethanol, to the aqueous colloidal solution [3]. When a particle is hydrophilic, its contact angle at the water|oil interface is less than 90° and consequently adsorption at the interface does not take place. When its contact angle approaches 90°, the particle prefers to adsorb in order to decrease the interfacial energy between the two phases. Previous works have shown that the addition of alcohols brings the contact angle of NPs close to 90° leading to their entrapment at the water|oil interface [3–5].

Other approaches to induce such interfacial nanoparticle assemblies have also been reported. Su et al. [6] showed that small NPs can be assembled at the interface upon applying a potential bias. For small mercaptosuccinic acid (MSA) stabilized Au NPs (1.5 nm ± 0.4 nm), differential capacitance and quasi-elastic laser scattering (QELS) measurements provided clear evidence that the surface concentration of the Au NPs at the liquid|liquid boundary is reversibly controlled by the applied potential. Reversible adsorption at the ITIES was also observed with larger citrate-stabilized gold core-silver shell NPs (16–20 nm) through second harmonic generation (SHG) measurements [7]. However, for gold NPs of this size, the weakness of the surface charge quickly induced the irreversible aggregation of the NPs at the liquid|liquid interface yielding some mirror like films on the interface.

The formation of Au nanocrystalline films by in-situ reduction at the liquid|liquid interface has been also investigated. The suggested mechanism is a L/L interfacial reaction (LLIR) [8] that allows interfacial nucleation and interfacial deposition of the Au NPs occurring along with the adsorption of capping ligands obtained from the reagents and the cleavage of the reducing agent. Few techniques were used to investigate the formation and ordering of Au NPs in a LLIR. Sanyal et al. used the grazing incidence X-ray scattering (GIXS) to follow the evolution of the interfacial roughness and associated density profile across the water|toluene interface as the interfacial reaction progresses [9,10].

Herein, we investigate the electrochemical behaviour of citrate-stabilized gold nanoparticles prepared via a bulk reaction at water|1,2-dichloroethane (DCE) interface under different conditions.

2. Experimental section

The compositions of the electrolyte solutions for the blank cell are indicated in Cell 1. The organic supporting electrolyte, bis(triphenylphosphoranylidene) ammonium tetrakis-(pentafluorophenyl)borate (BTPPATPFB), was prepared as previously mentioned [11]. Experiments were carried out in a custom-built glass cell featuring a cylindrical vessel

* Corresponding author. Tel.: +41 21 693 31 45; fax: +41 21 693 36 67.
E-mail address: hubert.girault@epfl.ch (H.H. Girault).

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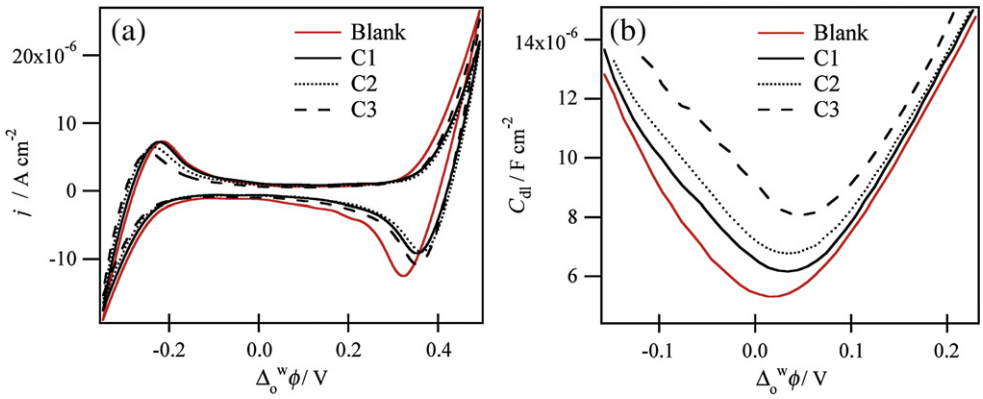

Fig. 1. (a) Cyclic voltammograms at a 50 mV/s scan rate (b) and capacitance measurements (2 Hz) for different concentrations (C) of the 16 nm gold NP solutions. Blank = Cell 1; C1 = 0.42 nM; C2 = 0.67 nM and C3 = 1.26 nM.

including two Luggin capillaries and two platinum counter-electrodes with a geometric cross-section of 1.53 cm^2. The volumes of the two immiscible phases are equal to about 3 mL each.

Ag	AgCl	NaCl 5.1 mM (aq)	BTPPATPFB 5 mM (DCE)	BTPPACl 1 mM LiCl 10 mM (aq)	AgCl	Ag	Cell 1

For the preparation of the gold nanoparticles solutions, hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$) was purchased from Sigma Aldrich, where citric acid and trisodium salt dehydrate from Fluka. Au NPs (average size of 16 nm) were synthesized using the wet Turkevich method [12]. The high nucleation rate yields narrow distributions of quasi-spherical shaped NPs. Transmission Electron Microscopy (TEM) and UV–visible spectra were used to analyse the size and the plasmon resonance band of the 16 nm prepared particles.

The interfacial capacitance was measured using an Ivium compactstat and Autolab PGSTAT128 N with their respective software at a frequency of 2 Hz. In the absence of any faradaic process, the liquid|liquid interface is modelled as a resistance R_s and an interfacial capacitance C_{dl} in series. The frequency used to make the measurements is such that the phase shift is about 90° and that the imaginary part of the impedance is directly proportional to the reciprocal of the capacitance.

3. Results and discussion

Fig. 1a shows cyclic voltammograms (CVs) of the potential window performed for different concentrations of 16 nm citrate-coated gold nanoparticles in the aqueous phase. As can be observed, the presence of gold nanoparticles at different bulk concentrations has little effect on the CVs, and no formation of a metallic film can be observed by eye. However, significant changes are noticed in the capacitance curves as clearly shown in Fig. 1b.

First of all, we can observe an increase of the capacitance at negative Galvani potential differences whereas the capacitance remains unaltered at positive values. These data therefore suggest that the negatively charged citrate-coated gold nanoparticles do adsorb at negative potentials. Usually, when amphiphilic aqueous anions adsorb at the interface, we can observe a decrease of capacitance. Here, the increase of capacitance can result from a higher counter ion surface charge density imposed by the charge density at the surface of the gold NPs, and also perhaps by an increase of the interfacial corrugation as shown schematically in Fig. 2a [13]. Indeed, Daikhin et al. reported that corrugation leads to an increase in capacitance, as compared with the Gouy–Chapman capacitance for a flat interface [14,15]. Furthermore, it has been shown that charging the interface gives rise to larger "dynamic corrugation" that immediately leads to increased values of capacitance [16]. In Fig. 1b, the minimum of capacitance is shifted to more positive potentials with increasing NP concentrations indicating the adsorption of negatively charged aqueous species. This effect was already noticed, both experimentally [6] and theoretically [17], for smaller Au NPs.

It has been shown that methanol injection is an effective way to induce the formation of a monolayer film with a metallic reflectance visible by eye when using citrate-stabilized Au NPs [18], as shown in Fig. 2b. Here, we have added methanol to the electrochemical cell just in presence of supporting electrolytes (see Cell 1), using a syringe to inject 300 μL close to the interface from the aqueous side as usually done to form metallic films, and the cell is left at least 30 min undisturbed in order to reach equilibrium. Fig. 3a–b shows cyclic voltammograms and capacitance curves, recorded before and after methanol injection.

The main effect of methanol is to induce higher transfer currents on the extremities of the potential window, particularly for the transfer of Na^+ at positive potential values. This could be due to a lowering of the Gibbs energy of transfer of Na^+ upon addition of

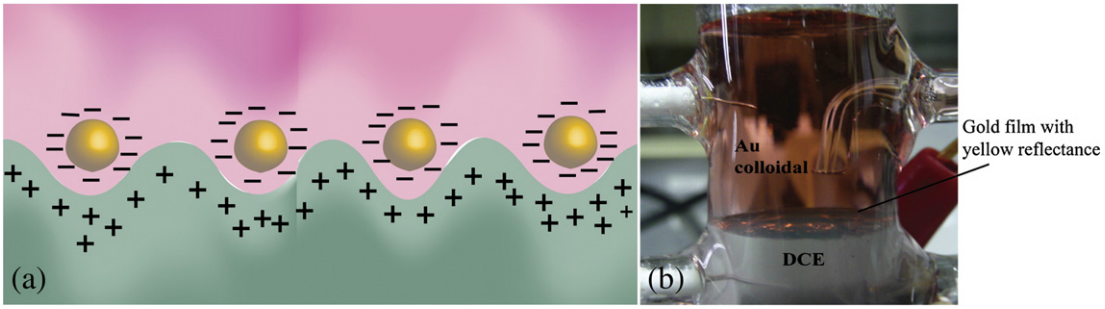

Fig. 2. (a) Schematic of the interface in the presence of adsorbed citrate-coated gold nanoparticles (b) a photograph of the methanol-induced gold film with metallic reflectance at the water|DCE interface.

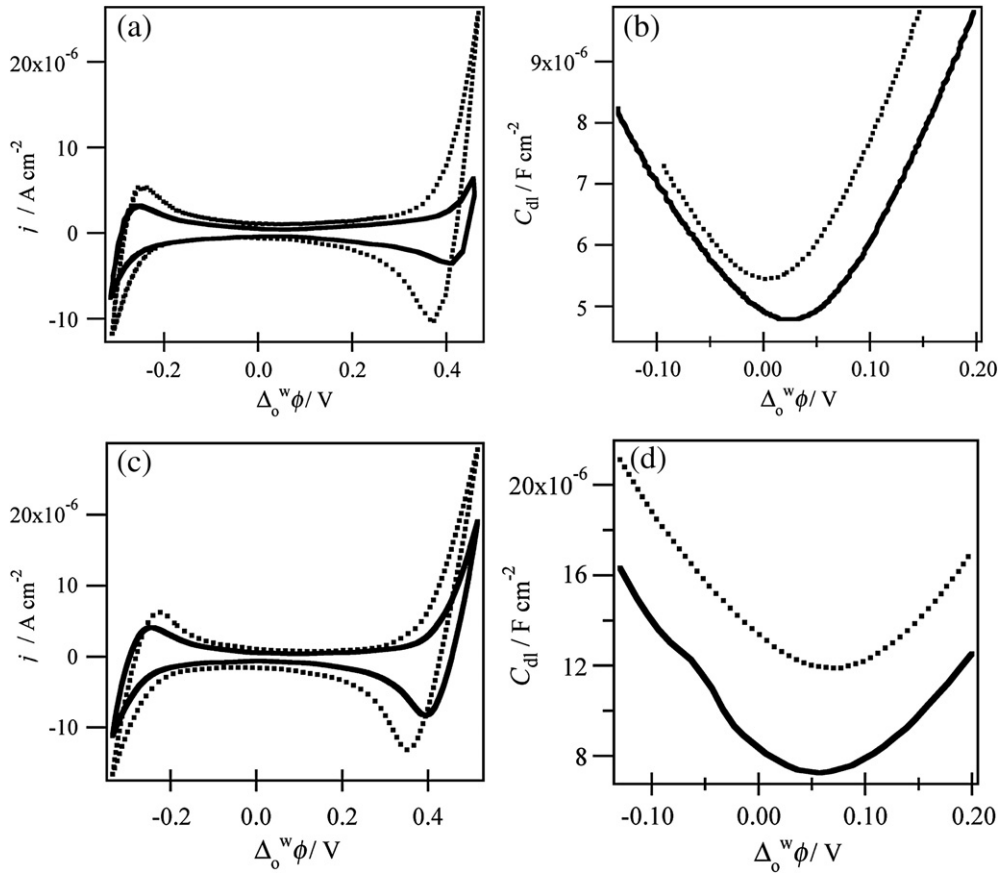

Fig. 3. (a) Cyclic voltammograms at 100 mV/s scan rate and (b) capacitance measurements (2 Hz) of the blank solution. (c) Cyclic voltammograms at 100 mV/s scan rate and (d) capacitance measurements (2 Hz) of 16 nm Au sol|DCE solution. Continuous lines: without methanol; dashed lines: 30 min after methanol injection.

methanol. The capacitance curve changes also, with a slight shift of the minimum to negative potentials associated with an increase in the capacitance value. Within the framework of the Gouy–Chapman model, where the capacitances of the adjacent phase are given by:

$$C^w = \frac{F}{RT}\left(2RT\varepsilon^w\varepsilon_0 c^w\right)^{\frac{1}{2}}\cosh\left(\frac{F\phi^w}{2RT}\right) \quad (1)$$

$$C^o = \frac{F}{RT}\left(2RT\varepsilon^o\varepsilon_0 c^o\right)^{\frac{1}{2}}\cosh\left(\frac{F\phi^w}{2RT}\right) \quad (2)$$

and the total capacitance at the interface given by

$$\frac{1}{C} = \frac{1}{C^o} + \frac{1}{C^w} \quad (3)$$

one could think that the observed increase of the interfacial capacitance is due to an increase of the relative permittivity of the organic phase. However, the partition coefficient of methanol between 1,2-dichloroethane and water, equal to 0.0623 at 25 °C [19], implies that methanol has little effect on the composition of the organic phase. Furthermore, the variation in the relative permittivity of the aqueous phase is negligible for a 10% volume ratio of methanol in water [20]. So this increase could be related to the formation of a more diffuse interface. Of course, this diffuse interface should be analysed by a mean field model as used recently by Schlossman et al. to analyse X-ray reflectivity data [21].

The effect of methanol injection when the aqueous phase contains citrate-coated gold nanoparticles is shown in Fig. 3c–d. Again, on the CVs we can only observe an increase of the sodium ion transfer

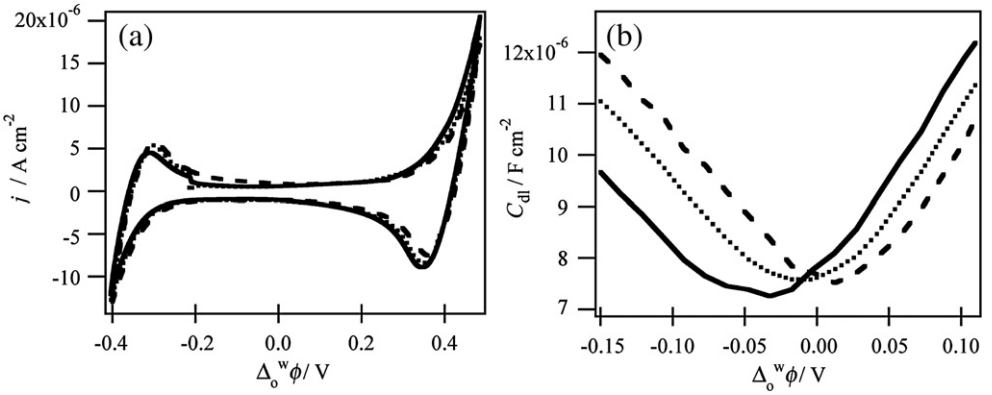

Fig. 4. (a) Cyclic voltammograms at 50 mV/s scan rate (b) and capacitance measurements (2 Hz) of 16 nm Au NP sol|DCE solutions. Solid line: no pre-polarisation, dots: polarisation at −0.2 V during 2 h, dashes: polarisation at −0.2 V for 2 h followed by polarisation at 0.2 V also for 2 h.

currents at positive potentials. The main difference appears on the capacitance curves. The minimum of the capacitance curves is increased by almost $4 \cdot 10^{-6}$ F/cm^2 whereas without nanoparticles, the increase observed in Fig. 3b was only $0.8 \cdot 10^{-6}$ F/cm^2. We can therefore conclude that the formation of a metallic film visible by eye results in a large increase of the capacitance that can be used as an in-situ tool to monitor the film formation.

Another way to induce adsorption at the interface for smaller nanoparticles is to polarise the interface [6]. Fig. 4 shows the effect of polarising the interface at −0.2 V where no ion transfer reaction takes place and where citrate-coated gold nanoparticles were seen to adsorb (see Fig. 1). As can be observed, the potential window is not affected by this pre-polarisation, but the capacitance curve changes with an increase of capacitance and a shift of the minimum towards positive potentials as in Fig. 1 when increasing the NP concentration. However, the capacitance increase is not as large as with methanol injection, and no metallic reflectance could be observed by eye. We have then tried to see if polarising the interface at 0.2 V would force the adsorbed NPs to desorb, but surprisingly the capacitance kept increasing and the minimum kept moving towards more positive potentials. It therefore seems that time is more important than interface polarisation in controlling the adsorption.

4. Conclusion

Cyclic voltammograms and capacitance measurements at polarised liquid|liquid interfaces can be used to monitor nanoparticles adsorption. Surprisingly, this adsorption results in an increase of capacitance that can be attributed to a corrugation of the interface accompanied by an increase of the local ionic strength associated to the charge carried by the metallic nanoparticles. A theoretical framework is necessary to make these measurements quantitative, but the method appears promising as a tool to monitor nanoparticle assemblies.

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